

1                   **PROCESS FOR MAKING GROUP II METAL CARBONATED,**  
2                   **OVERBASED MANNICH CONDENSATION PRODUCTS**  
3                   **OF ALKYLPHENOLS**

4                   FIELD OF THE INVENTION

5   This invention is directed to a novel process for making Group II metal  
6   carbonated, overbased Mannich condensation products of alkylphenols,  
7   which process uses ethylene carbonate as both a source of carbon dioxide  
8   and ethylene glycol. In particular, under the reaction conditions using  
9   ethylene carbonate in the present invention, overbasing of Mannich  
10   condensation products of alkylphenols is possible while at the same time  
11   viscosity of the carbonated, overbased Mannich condensation products of  
12   alkylphenols remains within acceptable levels, typically under 1000 cSt at  
13   100°C. This invention is also directed to a process for making Group II metal  
14   carbonated, overbased Mannich condensation products of alkylphenols,  
15   which process uses carbon dioxide and ethylene glycol. The present  
16   invention is also directed to a detergent-dispersant antioxidant additive  
17   composition comprising Group II metal carbonated, overbased Mannich  
18   condensation products of alkylphenols, wherein the Group II metal  
19   carbonated, overbased Mannich condensation products of alkylphenols have  
20   a CO<sub>2</sub> to Ca ratio of at least 0.01.

21   The present invention is also directed to a lubricating oil additive comprising  
22   Group II metal carbonated, overbased Mannich condensation products of  
23   alkylphenols, which is low in sulfur content, typically less than 0.3 percent as  
24   measured by ASTM Test No. D 4951-92.

25   The present invention is also directed to a Mannich condensation product  
26   comprising a reaction product of an alkylphenol, an aldehyde and  
27   N-phenyl-1,4-phenylene diamine.

1

## BACKGROUND OF THE INVENTION

2 The operation of diesel and spark ignition internal combustion engines is  
3 typically accompanied by the formation of sludge, lacquer and resinous  
4 deposits which adhere to the moving engine parts and thereby reduce engine  
5 efficiency. In order to prevent or reduce the formation of these deposits, a  
6 wide variety of chemical additives have been developed for incorporation into  
7 lubricating oils. These additives are commonly referred to as detergents and  
8 dispersants. Dispersants have the ability to keep deposit forming materials  
9 suspended in the oil so as to retard deposit formation during engine operation.  
10 Detergents have the ability to remove pre-existing deposits from the engine  
11 during engine operation and to neutralize acids in railroad, marine and  
12 automotive engines.

13 A large number of railroad and tugboat diesel engines use silver-plated  
14 bearings. As a result, the lubricating oil requires acceptable silver wear  
15 control and corrosion performance in addition to deposit control and alkalinity.  
16 Mannich bases and their salts have been known to be effective to protect  
17 silver bearing parts in such engines without the disadvantages associated  
18 with the use of chlorinated and dithiophosphate additives.

19 Mannich bases and their salts are also known to be particularly useful in  
20 lubricating oils, fuels, greases and plastics as antioxidants. Hydrocarbon  
21 materials are highly susceptible to chemical action on aging, exposure to  
22 sunlight and in their normal use. Such oxidation can lead to the deposit of  
23 undesirable residues in lubricants, fuels and greases and to discoloration of  
24 plastics.

25 Frequently, the inclusion of additives in lubricating oils and fuels to control  
26 deposits, wear and oxidation cause compatibility problems. In addition, it is  
27 uneconomical to add many additives in order to achieve all these functions.

1 Thus, there is a great need for the development of a single multifunctional  
2 agent that will perform all these desired functions.

3 One class of lubricating oil additives typically used as dispersants, detergents,  
4 oxidation inhibitors and anti-wear additives are Mannich condensation  
5 products of an alkylphenol, an aldehyde and an amine.

6 Various Mannich condensation products known in the prior art as lubricating  
7 oil additives are metal salts. Currently, there is no carbonation process in the  
8 prior art for making Group II metal carbonated, overbased Mannich  
9 condensation products of alkylphenol which have a high alkalinity reserve for  
10 neutralizing acids in engines and at the same time have acceptable viscosity.  
11 It is believed that the carbonate, overbased Mannich condensation products  
12 of alkylphenols of the present invention are superior to the prior art salts of  
13 Mannich condensation products of alkylphenols for providing the functions of  
14 detergent-dispersants, anti-wear and oxidation agents in one additive  
15 because of their greater alkalinity reserve and acceptable viscosities.

16 The ability of additive compositions to neutralize acids in engines can be  
17 measured by determining the total base number (TBN) or the alkalinity  
18 reserve of the composition. Higher TBNs reflect a greater capacity for these  
19 compositions to neutralize acids generated during engine operation.  
20 However, the TBN of a composition is directly related to the amount of diluent  
21 oil present. Thus, more concentrated compositions will have a higher TBN  
22 than those containing more diluent.

23 The preparation of Group II metal salts of Mannich condensation products of  
24 alkylphenol compositions is well known in the art. A number of patents have  
25 discussed processes for making Group II metal salts of the Mannich  
26 condensation products of alkylphenols, but none have included a carbonation  
27 step in the process.

1 For example, U.S. Pat. No. 3,036,003 discloses a process for making a metal  
2 salt of a condensation product of an alkylene polyamine, an aldehyde and  
3 substituted phenol.

4 U.S. Pat No. 3,340,190 discloses the preparation of a mixture of the exactly  
5 neutralized calcium salt of N,N'-bis(alkyl substituted hydroxybenzyl) alkylene  
6 diamine and a bis (alkenylsuccinimide) of polyalkylene polyamine or of a urea  
7 condensation derivative of polyalkylene polyamine,  
8 N,N'-bis(polyazalkylamino) ureylene.

9 U.S. Pat. No. 3,586,629 discloses the preparation of salts obtained by  
10 reacting the condensation product of an alkyl hydroxy aromatic compound, an  
11 aldehyde and an amine or alkali metal salt thereof with a metal base. These  
12 salts provide excellent detergency characteristics to an organic industrial fluid.

13 U.S. Pat. No. 3,798,163 teaches a method for inhibiting exhaust valve  
14 recession in natural gas fueled internal combustion engines with the use of  
15 composition comprising a lubricating oil, a metal sulfonate and at least one  
16 metal salt of a condensation product of an alkylene polyamine, an aldehyde  
17 and a substituted phenol.

18 U.S. Pat. No. 3,958,624 discloses an improved anti-fouling additive for use in  
19 organic heat transfer fluids comprising a combination of a barium overbased  
20 calcium sulfonate and a phenolic antioxidant, an alkaline earth aminophenate.

21 U.S. Pat. No. 4,025,316 discloses the preparation of polymeric alkyl-hydroxy  
22 benzyl N-substituted amines having a high degree of ring formation derived  
23 from the condensation reaction of C<sub>8</sub>-C<sub>40</sub> aliphatic alkyl substituted hydroxy  
24 aromatic, an aldehyde and an amine.

25 U.S. Pat. No. 4,088,586 discloses the preparation of salts of Mannich bases  
26 from tetrapropenylphenol, formaldehyde and diethylenetriamine when the

1 molar ratio of the reactant is 1 mole tertapropenylphenol to 0.5 to 0.85 mole  
2 formaldehyde to at least 0.3 mole of diethylenetriamine having outstanding  
3 viscosity and alkalinity value properties.

4 U.S. Pat. No. 4,140,492 discloses the preparation of borated derivatives of  
5 oil-soluble Mannich bases for use in combination with coadditive  
6 hydrocarbons for flow improvers for middle distillate fuel oils.

7 U.S. Pat. Nos.4,157,308 discloses the preparation of Mannich base  
8 compositions and their metal salts from phenolic mixtures consisting of phenol  
9 alkylated with a propylene tetramer and phenol alkylated with a straight-chain  
10 alpha-olefin.

11 U.S. Pat. No. 4,231,759 discloses a liquid hydrocarbon combustion fuel  
12 containing an additive composition comprising the Mannich condensation  
13 product of a high molecular weight alkyl-substituted hydroxyaromatic  
14 compound wherein the alkyl group has a molecular weight of from about 600  
15 to about 3,000.

16 U.S. Pat. No. 4,655,949 discloses novel lubricating oil composition comprising  
17 an organometallic additive containing a metal selected from Groups I, Ib and  
18 VIII chelated with the reaction product of formaldehyde, an amino acid and a  
19 phenol.

20 U.S. Pat. Nos. 4,734,211; 4,764,296 and 4,820,432 disclose a lubricating oil  
21 composition for railway diesel engines which contains calcium salt of Mannich  
22 reaction product among other additives. The Mannich base is prepared using  
23 an alkyl substituted hydroxy aromatic compound, specifically para-alkyl  
24 phenol. The TBN of the product was approximately 160.

25 Typically, Mannich bases are prepared by reacting an alkylphenol with an  
26 aldehyde and an amine wherein the amine is a primary or secondary aliphatic

1 or aromatic amine or polyamine, and the aldehyde is an aliphatic or aromatic  
2 aldehyde. The alkyl group of the phenol can be straight-chain or branched-  
3 chain. Optionally, a promoter may be used during the condensation reaction.

4 The prior art process for making the metal salt of the Mannich bases is  
5 typically by the addition of a metal oxide, hydroxide or hydroperoxide.  
6 Optionally, ethylene glycol is added to the reaction mixture to promote the salt  
7 formation.

## 8 SUMMARY OF THE INVENTION

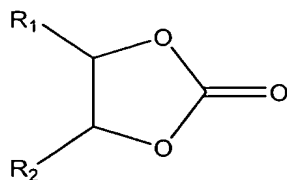
9 The present invention is directed to a novel process for making Group II metal  
10 carbonated, overbased Mannich condensation products of alkylphenols,  
11 which process uses ethylene carbonate as both a source of carbon dioxide  
12 and ethylene glycol. In particular, under the reaction conditions using  
13 ethylene carbonate in the present invention, overbasing, as defined herein, of  
14 Mannich alkylphenols is possible while at the same time the viscosity of the  
15 carbonated, overbased Mannich condensation products of alkylphenols  
16 remains within acceptable levels, typically under 1000 cSt at 100°C. This  
17 invention is also directed to a process for making Group II metal carbonated,  
18 overbased Mannich condensation products of alkylphenols, which process  
19 uses carbon dioxide and ethylene glycol. The present invention is also  
20 directed to a detergent-dispersant antioxidant additive composition comprising  
21 Group II metal carbonated, overbased Mannich condensation products of  
22 alkylphenols, wherein the Group II metal carbonated, overbased Mannich  
23 condensation products of alkylphenols have a CO<sub>2</sub> to Ca ratio of at least 0.01.

24 The present invention is also directed to a lubricating oil additive comprising  
25 Group II metal carbonated, overbased Mannich condensation products of  
26 alkylphenols, which is low in sulfur content, typically less than 0.3 percent as  
27 measured by ASTM Test No. D 4951-92. It is believed that the sulfur content  
28 in the Group II metal carbonated, overbased Mannich condensation products

1 of alkylphenols of the present invention is contributed by the diluent used in  
2 the preparation of the Group II metal carbonated, overbased Mannich  
3 condensation products of alkylphenols.

4 In particular, the process of the present invention for preparing Group II metal  
5 carbonated, overbased Mannich condensation products of alkylphenols  
6 comprises:

7 forming a reaction mixture by combining a Mannich condensation product of  
8 an alkylphenol wherein the alkyl group contains a sufficient number of carbon  
9 atoms to render oil-soluble the resulting Group II metal carbonated,  
10 overbased Mannich condensation product of alkylphenol, a Group II metal  
11 oxide, hydroxide or C<sub>1</sub>-C<sub>6</sub> alkoxide, in the presence of a promoter and  
12 optionally a second promoter, and an alkylene carbonate selected from  
13 ethylene carbonate or a mono-alkyl or di-alkyl substituted ethylene carbonate,  
14 said alkylene carbonate having the following structure:



16 wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or alkyl containing one to  
17 three carbon atoms; and wherein the combining is carried out for a time and  
18 at a temperature sufficient to form in situ carbon dioxide and alkylene glycol,  
19 or a reacting equivalent, to form a product comprising a Group II metal  
20 carbonated, overbased Mannich condensation product of alkylphenol.

21 In the alkylene carbonate structure above, preferably one of R<sub>1</sub> and R<sub>2</sub> is  
22 hydrogen and the other is hydrogen or methyl. In other words, the alkylene  
23 carbonate is preferably ethylene carbonate or propylene carbonate. More  
24 preferably, R<sub>1</sub> and R<sub>2</sub> are both hydrogen; that is, the alkylene carbonate is  
25 ethylene carbonate.

1 In another embodiment, the Mannich condensation product of alkylphenol  
2 used in the process of the present invention as described above may be  
3 replaced with a Group II metal salt.

4 A further embodiment of the present invention is directed to a process for  
5 making Group II metal carbonated, overbased Mannich condensation  
6 products of alkylphenols, in which process a C<sub>2</sub>-C<sub>10</sub> alkylene glycol and  
7 carbon dioxide replace the alkylene carbonate. Preferably, the C<sub>2</sub>-C<sub>10</sub>  
8 alkylene glycol is ethylene glycol.

9 The alkylene carbonate is added to the reaction mixture over a time period of  
10 about 15 minutes to about 120 minutes. Preferably, the alkylene carbonate is  
11 added to the reaction mixture over a time period of about 30 minutes to about  
12 90 minutes, and more preferably the alkylene carbonate is added to the  
13 reaction mixture over a time period of about 40 minutes to about 60 minutes.

14 The promoter used in the process of the present invention is typically a C<sub>2</sub>-C<sub>10</sub>  
15 alkylene glycol.

16 The promoter optionally used in the process of the present invention may  
17 typically include water, a C<sub>1</sub>-C<sub>5</sub> mono- or di-alcohol or a C<sub>2</sub>-C<sub>10</sub> alkylene glycol  
18 or a mixture thereof. Preferably, the promoter optionally used is a C<sub>2</sub>-C<sub>10</sub>  
19 alkylene glycol, and more preferably the promoter optionally used is water.

20 Optionally, the process of the present invention further comprises the step of  
21 recovering the product by filtering the reaction mixture to remove sediment.

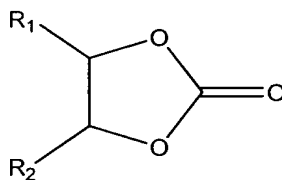
22 An alternate embodiment of the present process for preparing Group II metal  
23 carbonated, overbased Mannich condensation products of alkylphenols  
24 comprises the steps of:

25 (a) forming a reaction mixture by combining a Mannich condensation  
26 product of alkylphenol wherein the alkyl group contains a sufficient



number of carbon atoms to render oil-soluble the resulting Group II metal carbonated, overbased Mannich condensation product of alkylphenol, a Group II metal oxide, hydroxide or C<sub>1</sub>-C<sub>6</sub> alkoxide, a promoter and optionally a second promoter; and

(b) contacting said reaction mixture with an alkylene carbonate selected from ethylene carbonate or a mono-alkyl or di-alkyl substituted ethylene carbonate, said alkylene carbonate having the following structure:



wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or alkyl containing one to three carbon atoms; and wherein the contacting is carried out for a time and at a temperature sufficient to form in situ carbon dioxide and alkylene glycol, or a reacting equivalent, to form a product comprising a Group II metal carbonated, overbased Mannich condensation product of alkylphenol.

In the alkylene carbonate structure above, preferably one of R<sub>1</sub> and R<sub>2</sub> is hydrogen and the other is hydrogen or methyl. In other words, the alkylene carbonate is preferably ethylene carbonate or propylene carbonate. More preferably, R<sub>1</sub> and R<sub>2</sub> are both hydrogen; that is, the alkylene carbonate is ethylene carbonate.

The Mannich condensation product of alkylphenol used in the alternate embodiment of the process of the present invention as described above may be replaced with a Group II metal salt.

1 A further embodiment of the alternate embodiment is directed to a process for  
2 making Group II metal carbonated, overbased Mannich condensation  
3 products of alkylphenols, in which process a C<sub>2</sub>-C<sub>10</sub> alkylene glycol and  
4 carbon dioxide replace the alkylene carbonate in step (b). Preferably, the  
5 C<sub>2</sub>-C<sub>10</sub> alkylene glycol is ethylene glycol.

6 The alkylene carbonate is added to the reaction mixture over a time period of  
7 about 15 minutes to about 120 minutes. Preferably, the alkylene carbonate is  
8 added to the reaction mixture over a time period of about 30 minutes to about  
9 90 minutes, and more preferably the alkylene carbonate is added to the  
10 reaction mixture over a time period of about 40 minutes to about 60 minutes.

11 The promoter used in step (a) of the above process of the present invention is  
12 a C<sub>2</sub>-C<sub>10</sub> alkylene glycol.

13 The promoter optionally used in step (a) of the process is typically water, a  
14 C<sub>1</sub>-C<sub>5</sub> mono- or di-alcohol or a C<sub>2</sub>-C<sub>10</sub> alkylene glycol or a mixture thereof.  
15 Preferably, the promoter optionally used is a C<sub>2</sub>-C<sub>10</sub> alkylene glycol, and more  
16 preferably the promoter optionally used is water.

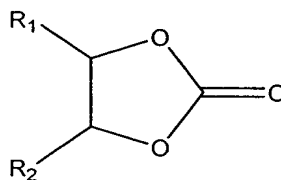
17 Optionally, the process of this embodiment further comprises the step of  
18 recovering the product by filtering the reaction mixture to remove sediment.

19 Another embodiment of the present process for preparing Group II metal  
20 carbonated, overbased Mannich condensation products of alkylphenols  
21 comprises the steps of:

22 (a) forming a first reaction mixture by combining an alkylphenol  
23 wherein the alkyl group contains a sufficient number of carbon  
24 atoms to render oil-soluble the resulting Group II metal carbonated,  
25 overbased Mannich condensation product of alkylphenol, an  
26 aldehyde and an amine and a promoter optionally used;

1 (b) contacting said first reaction mixture with a second reaction mixture  
2 comprising a Group II metal oxide, hydroxide or C<sub>1</sub>-C<sub>6</sub> alkoxide; an  
3 inert hydrocarbon diluent, a promoter and optionally a second  
4 promoter to form a third reaction mixture; and

5 (c) contacting said third reaction mixture with an alkylene carbonate  
6 selected from ethylene carbonate or a mono-alkyl or di-alkyl  
7 substituted ethylene carbonate, said alkylene carbonate having the  
8 following structure:



9  
10 wherein R<sub>1</sub> and R<sub>2</sub> are independently hydrogen or alkyl containing  
11 one to three carbon atoms; and wherein said contacting is carried  
12 out for a time and at a temperature sufficient to form in situ carbon  
13 dioxide and alkylene glycol, or a reacting equivalent, to form a  
14 product comprising a Group II metal carbonated, overbased  
15 Mannich condensation product of alkylphenol.

16 In the alkylene carbonate structure above, preferably one of R<sub>1</sub> and R<sub>2</sub> is  
17 hydrogen and the other is hydrogen or methyl. In other words, the alkylene  
18 carbonate is preferably ethylene carbonate or propylene carbonate. More  
19 preferably, R<sub>1</sub> and R<sub>2</sub> are both hydrogen; that is, the alkylene carbonate is  
20 ethylene carbonate.

21 In step (a) of the above embodiment of the present invention, the temperature  
22 of reaction mixture is in the range of about 35°C to about 170°C.

23 A further embodiment is directed to a process for making Group II metal  
24 carbonated, overbased Mannich condensation products of alkylphenols, in

1 which process a C<sub>2</sub>-C<sub>10</sub> alkylene glycol and carbon dioxide replace the  
2 alkylene carbonate in step (c). Preferably, the C<sub>2</sub>-C<sub>10</sub> alkylene glycol is  
3 ethylene glycol.

4 The alkylene carbonate is added to the reaction mixture over a time period of  
5 about 15 minutes to about 120 minutes. Preferably, the alkylene carbonate is  
6 added to the reaction mixture over a time period of about 30 minutes to about  
7 90 minutes, and more preferably the alkylene carbonate is added to the  
8 reaction mixture over a time period of about 40 minutes to about 60 minutes.

9 The promoter used in step (b) of the process of the above present  
10 embodiment is a C<sub>2</sub>-C<sub>10</sub> alkylene glycol.

11 The promoter optionally used in step (b) of the above present embodiment is  
12 typically water, a C<sub>1</sub>-C<sub>5</sub> mono- or di-alcohol or a C<sub>2</sub>-C<sub>10</sub> alkylene glycol or a  
13 mixture thereof. Preferably, the promoter is a C<sub>2</sub>-C<sub>10</sub> alkylene glycol, and  
14 more preferably the promoter is water.

15 In step (a), the amine may be an aliphatic amine, an aromatic amine, a  
16 polyfunctional amine, such as ethanol amine, or mixtures thereof, containing  
17 at least one amino group characterized by the presence of at least one active  
18 hydrogen or methylene group, and wherein the amine contains only primary  
19 amino groups, only secondary amino groups, or both primary and secondary  
20 amino groups.

21 The aliphatic amine may be an alkylene diamine, a dialkylamine, a  
22 polyalkylene polyamine or mixtures thereof. The aromatic amine may be a  
23 single-ring aromatic amine or a double-ring aromatic amine.

24 In step (a), the aldehyde may be an aliphatic aldehyde, aromatic aldehyde, a  
25 heterocyclic aldehyde or mixtures thereof. Preferably, the aliphatic aldehyde

1 is formaldehyde or paraformaldehyde, the aromatic aldehyde is  
2 benzaldehyde, and the heterocyclic aldehyde is furfural.

3 The molar ratios of the alkylphenol, the aldehyde and the amine in step (a)  
4 are from about 1:1.8:1 to about 1:3:1.

5 The alkyl group of the alkylphenol may be straight-chain or branched-chain  
6 and will typically contain at least 10 carbon atoms, preferably from about  
7 12 carbon atoms to about 50 carbon atoms.

8 Preferably, the alkyl group of the alkylphenol contains from about 25 to about  
9 100 mole percent predominantly straight-chain alkyl groups containing from  
10 about 15 to about 35 carbon atoms and from about 75 to about 0 mole  
11 percent branched-chain alkyl groups containing from about 9 to about  
12 18 carbon atoms. Preferably, the alkyl group of the alkylphenol contains from  
13 about 40 to about 70 mole percent predominantly straight-chain alkyl groups  
14 containing from about 15 to about 35 carbon atoms and from about 60 to  
15 about 30 mole percent branched-chain alkyl groups containing from about 9 to  
16 about 18 carbon atoms.

17 In a preferred embodiment, the alkyl group of the alkylphenol is attached  
18 predominantly at the para position of the phenol ring. Preferably, the  
19 alkylphenol containing the para attachment of the alkyl group is from about  
20 70 to about 95 weight percent of the total alkylphenol. More preferably, the  
21 alkylphenol containing the para attachment of the alkyl group is from about  
22 80 to about 95 weight percent of the total alkylphenol.

23 The Group II metal oxide, hydroxide or C<sub>1</sub>-C<sub>6</sub> alkoxide is selected from the  
24 group consisting of calcium, barium, and magnesium oxide, hydroxide or  
25 C<sub>1</sub>-C<sub>6</sub> alkoxide and mixtures thereof. Preferably, the Group II metal oxide,  
26 hydroxide or C<sub>1</sub>-C<sub>6</sub> alkoxide is calcium hydroxide.

1 Optionally, the process of this embodiment further comprises the step of  
2 recovering the product by filtering the reaction mixture to remove sediment.

3 The carbonation processes of the instant invention are particularly useful for  
4 preparing Group II metal carbonated, overbased Mannich condensation  
5 products of alkylphenols possessing a CO<sub>2</sub> to Ca ratio of at least about 0.01,  
6 and preferably in the range of about 0.1 to about 0.6, and more preferably in  
7 the range of about 0.3 to about 0.5.

8 The processes of the present invention may be carried out in a batch or a  
9 continuous process. It is believed that small changes in pressure will have  
10 little effect on the carbonation process of the present invention.

11 The present invention is also directed to a detergent-dispersant and  
12 antioxidant additive comprising Group II metal carbonated, overbased  
13 Mannich condensation products of alkylphenols, said additive having a CO<sub>2</sub> to  
14 Ca ratio of at least about 0.01, and preferably in the range of about 0.1 to  
15 about 0.6, and more preferably in the range of about 0.3 to about 0.5.

16 The detergent-dispersant antioxidant additive of the present invention  
17 comprises Group II metal carbonated, overbased Mannich condensation  
18 product of alkylphenol wherein the Mannich alkylphenol is a condensation  
19 product of an alkylphenol, an aldehyde and an aliphatic, an aromatic, a  
20 polyfunctional amine or mixtures thereof, said additive having a CO<sub>2</sub> to Ca  
21 ratio of at least about 0.01, and preferably in the range of about 0.1 to about  
22 0.6, and more preferably in the range of about 0.3 to about 0.5.

23 The present invention is also directed to a Mannich condensation product  
24 comprising a reaction product of an alkylphenol, an aldehyde and  
25 N-phenyl-1,4-phenylene diamine wherein the alkyl group of the alkylphenol is  
26 a straight-chain alkyl group or branched-chain alkyl group containing from  
27 about 10 carbon atoms to about 50 carbon atoms. Preferably, the alkyl group

1 of the alkylphenol has about 12 carbon atoms to about 24 carbon atoms. The  
2 aldehyde is an aliphatic aldehyde, aromatic aldehyde, a heterocyclic aldehyde  
3 or mixtures thereof. Preferably, the aliphatic aldehyde is paraformaldehyde or  
4 formaldehyde. More preferably, the alkyl group of the alkylphenol has about  
5 12 carbon atoms, the aldehyde is paraformaldehyde, and the amine is  
6 N-phenyl-1,4-phenylene diamine in the Mannich condensation product of this  
7 invention.

## 8 DETAILED DESCRIPTION OF THE INVENTION

### 9 DEFINITIONS

10 As used herein, the following terms have the following meanings unless  
11 expressly stated to the contrary:

12

13 The term "alkoxide" means a compound which can be formed as the reaction  
14 product of an alcohol and a reactive metal.

15

16 The term "alkylene glycol" means an aliphatic diol having two hydroxy groups  
17 on adjacent carbon atoms.

18

19 The term "alkylphenol" means a phenol group having one or more alkyl  
20 substituents, at least one of which has a sufficient number of carbon atoms to  
21 impart oil solubility to the phenol.

22

23 The term "carbonated, overbased Mannich condensation products of  
24 alkylphenols" means the products obtained after carbonation and overbasing,  
25 as described in the process of the present invention, of Mannich bases  
26 prepared by reacting an alkylphenol with an aldehyde and an amine wherein  
27 the amine is a primary or secondary aliphatic or aromatic amine or polyamine,  
28 the aldehyde is an aliphatic or aromatic aldehyde.

29

1 Use of the term "ethylene carbonate" includes alkyl-substituted alkylene  
2 carbonate, such as propylene carbonate and the like.  
3  
4 The term "overbased" as used herein describes those Group II metal  
5 carbonated, overbased Mannich condensation products of alkylphenols in  
6 which the ratio of carbon dioxide to calcium is at least 0.01 and may be as  
7 high as 0.6.  
8  
9 The term "promoter" means a C<sub>2</sub>-C<sub>10</sub> alkylene glycol capable of assisting in  
10 the carbonation step of the process of the present invention.  
  
11 The term "promoter optionally used" means any polar chemical, such as  
12 water, a C<sub>1</sub>-C<sub>5</sub> mono- or di-alcohol or ethylene glycol or a mixture thereof, that  
13 is capable of assisting in the process of the present invention.  
14  
15 The term "one or more promoters" means a promoter or a promoter optionally  
16 used as defined herein.  
17  
18 The term "reacting equivalent" means any material equivalent to ethylene  
19 glycol and carbon dioxide, such as the carbonic acid half ester.  
20  
21 Sulfur content was measured by ASTM Test No. D 4951-92.  
  
22 The term "Total Base Number" or "TBN" refers to the amount of base  
23 equivalent to milligrams of KOH in one gram of sample. The TBN of a sample  
24 can be determined by ASTM Test No. D 2896 or any other similar procedure.  
25  
26 Calcium content of the carbonated, overbased Group II metal Mannich  
27 condensation products of alkylphenols was measured using the following  
28 procedure:  
29



1 Samples of 0.5 grams to 2.0 grams placed in 8 milliliter vials with plastic-lined  
2 screw caps and diluted with a solution of ortho-xylene that contains 8%  
3 mineral oil, 340D, and a 50 ppm Ag internal standard element. Analysis is  
4 done using the Inductively Coupled Plasma in an Inductively Coupled Plasma  
5 Optical Emission Spectrometer. Results are reported as parts per million  
6 (w/w) or weight percent.

7

8 Carbon dioxide content of the carbonated, overbased Group II metal Mannich  
9 condensation products of alkylphenols was measured using the following  
10 procedure:

11

12 Approximately 100 mg of sample is weighed into a test tube and acidified with  
13 p-toluene sulfonic acid to release CO<sub>2</sub>. The liberated gases are swept  
14 through several scrubbers to remove interfering species. The resultant gas  
15 stream is bubbled into a solution that contains mono-ethanol amine (MEA)  
16 and a pH sensitive indicator. The addition of CO<sub>2</sub> to the solution changes the  
17 pH, which changes the color of the indicator. The color change is sensed by  
18 a visible spectrophotometer, and a controlling coulometer generates hydroxyl  
19 ion at an electrode in the solution to bring the pH back to its original value.  
20 The titration charge is related back to the original amount of acid evolved  
21 carbon in the sample by means of Coulomb's law. The result is given as  
22 weight percent CO<sub>2</sub>.

23

24 Kinematic viscosity of the carbonated, overbased Group II metal Mannich  
25 condensation products of alkylphenols was measured using the following  
26 modified ASTM Test No. D 445:

27

28 A portion (1-5 milliliters) of sample is loaded into a calibrated Zeitfuchs  
29 cross-arm viscometer. The sample and viscometer are brought to thermal  
30 equilibrium by immersion in a temperature-controlled bath. The sample level  
31 is brought to a mark on the viscometer. The sample is induced to flow by  
32 applying a small momentary pressure; after the flow has begun, the sample

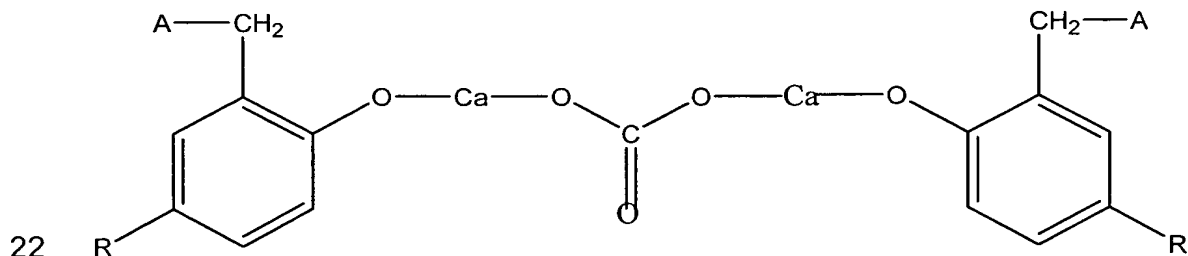
1 flows under gravity. The time is measured for the sample to flow between two  
2 marks on the viscometer. The time is related to the sample viscosity by  
3 means of the previously determined calibration constant. Results are  
4 reported as centistokes at 100°C.

5 Unless otherwise specified, all percentages are in weight percent and the  
6 pressure is atmospheric pressure.

7

8 It has been determined that the alkalinity reserve of the Group II metal  
9 Mannich alkylphenols can be increased by the addition of a carbonation step  
10 after the neutralization of the Group II metal Mannich condensation products  
11 of alkylphenols with calcium hydroxide. The term "overbased" as used herein  
12 describes those Group II metal Mannich condensation products of  
13 alkylphenols in which the ratio of carbon dioxide to calcium is at least 0.01  
14 and may be as high as 0.6. In contrast, the equivalent ratio of carbon dioxide  
15 to calcium is 0.0 in uncarbonated Group II metal Mannich condensation  
16 products of alkylphenol because the neutralization of Group II metal Mannich  
17 condensation products of alkylphenol is generally carried out with calcium  
18 hydroxide and without carbonation.

19 Without being bound by any theory, it is believed that one possible chemical  
20 structure of the Group II metal carbonated-overbased product of the  
21 carbonation step is as depicted below:



24 wherein R is alkyl and A is an amine or a polyamine.

1 Current automotive formulations require very low sulfur levels, less than  
2 0.3 percent, and future formulations may require even lower levels of sulfur.  
3 Thus, the additive itself must add little or no sulfur to the finished lubricating oil  
4 product. However, conventional detergent-dispersant additives, such as  
5 Group II metal overbased sulfurized alkylphenols, increase the sulfur content  
6 of the finished lubricating oil product because of the high sulfur content of the  
7 additive. The carbonated, overbased Mannich condensation products of  
8 alkylphenol additives of the present invention have the distinct advantage over  
9 the conventional detergent-dispersant additives in that the final sulfur content  
10 of the additives is below 0.3 percent, which sulfur content may be present in  
11 the diluent oil used for making the carbonated, overbased Mannich  
12 condensation products of alkylphenols. The carbonated, overbased Mannich  
13 condensation products of alkylphenols themselves do not contain sulfur.

14 As noted above, this invention is directed to a novel process for the rapid  
15 carbonation of Mannich condensation products of alkylphenols using ethylene  
16 carbonate or alkylene-substituted ethylene carbonate. We have discovered  
17 that the ethylene carbonate in the carbonation step for the preparation of  
18 carbonated, overbased Mannich condensation products of alkylphenols can  
19 be used as both a source of carbon dioxide and ethylene glycol. Under the  
20 reaction conditions using ethylene carbonate, rapid carbonation of Mannich  
21 condensation products of alkylphenols is feasible for the preparation of  
22 carbonated, overbased Mannich condensation products of alkylphenols which  
23 has not been possible in the prior art processes.

24

25 The carbonation of Mannich condensation products of alkylphenols using the  
26 processes of the present invention provide a product with good alkalinity  
27 reserve and acceptable viscosity compared to the prior art salts of Mannich  
28 condensation products of alkylphenols without any loss in the quality of the  
29 product. The chemical and physical properties of the product of the present  
30 process are also good, including high base content, low crude product  
31 sediment and fast filtration rates.

## EXAMPLES

### General Procedure for Examples

#### Preparation of Carbonated, Overbased Mannich Condensation Products of Alkylphenols

Below is described the procedure generally used for the preparation of carbonated, overbased Mannich condensation products of alkylphenols in accordance with the present invention. Specific amounts used in the preparation of Examples 1-46 and A-E are given in Tables I and VI.

Into a 4 liter, 5-neck resin kettle reactor equipped with metal baffle insert, a turbine blade mechanical stirrer and a reflux condenser (closed at the top), the following components were combined:

- 804.8 grams of C<sub>10</sub>-C<sub>15</sub> alkylphenol
- 7.5 grams of defoamer, polydimethylsiloxane, Dow Corning 200® purchased from Dow Corning
- 168.2 grams of paraformaldehyde
- 480.8 grams of 150 Neutral oil purchased from ExxonMobil, which contained 0.278 and 0.374 percent sulfur.

The contents of the reactor were stirred to 600 rpm and the temperature was ramped to 50°C and 88.4 grams of monomethylamine was added over a period of 1/2 hour. The temperature was ramped to 70°C to 95°C over the next 1 hour, cooling being employed if necessary to keep the temperature below 95°C. Next, the temperature was ramped to 140°C for 1/2 hour, and then held at 140°C for 1/2 hour. At the end of this time period, the vacuum was broken with air and 244.4 grams of 150 Neutral oil, which contained 0.278 and 0.374 percent sulfur, was added to the reactor. The reactor was cooled from 80°C to 90°C, and the following additional components were added to the reactor:



1 Table I below lists the components that were varied in Examples 1-29.

2

3

Table I

4

Ex.	Amount of Reaction Components Charge Mole Ratio relative to the Alkylphenol						
	Diethylene- triamine	Ethanol- amine	Monomethyl- amine	1,4- Phenylene -diamine	N,phenyl- 1,4- phenylene- diamine	Ethylene Glycol	Ethylene Carbonate
1	-	-	0.987	-	-	0.328	0.394
2	-	-	0.987	-	-	0.328	0.453
3	-	-	0.914	-	-	0.298	0.358
4	-	-	0.942	-	-	0.284	0.358
5	-	-	0.970	-	-	0.284	0.358
6	-	-	0.987	-	-	0.328	0.634
7	-	-	0.987	-	-	0.328	0.634
8	1.000	-	-	-	-	0.328	0.394
9	1.000	-	-	-	-	0.328	1.000
10	1.000	-	-	-	-	0.328	0.697
11	1.000	-	-	-	-	0.328	1.000
12	0.667	-	-	-	-	0.328	0.667
13	0.495	-	-	-	-	0.328	1.304
14	-	0.997	-	0.499	-	0.328	0.394
15	-	0.997	-	-	-	0.284	0.358
16	-	1.047	-	-	-	0.284	0.358
17	-	1.047	-	-	-	0.284	0.358
18	-	1.047	-	-	-	0.284	0.376
19	-	1.047	-	-	-	0.284	0.376
20	-	1.047	-	-	-	0.284	0.376
21	-	1.152	-	-	-	0.284	0.376
22	-	1.204	-	-	-	0.284	0.376
23	-	1.256	-	-	-	0.284	0.376
24	-	1.047	-	-	-	0.284	0.376
25	-	1.047	-	-	-	0.284	0.395
26	-	1.047	-	-	-	0.284	0.413
27	-	1.047	-	-	-	0.284	0.434
28	-	1.047	-	-	-	0.284	0.456
29	-	-	-	-	1.000	0.284	0.413

5

6

7 The results obtained for Examples 1-29 are given below in Tables II to V.

8

1 Table II shows the results obtained when monomethyl amine was used to  
2 make the Mannich bases.

3 Table II

4

Ex.	CO <sub>2</sub> /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
1	0.394	159	0.21	154	NA *
2	0.425	188	0.17	219	12.0
3	0.424	200	0.20	402	3.6
4	0.350	196	0.16	551	4.8
5	0.342	207	0.17	693	1.4
6	0.422	186	0.20	103	4.0
7	0.492	180	0.14	214	10.0

5  
6 \* Data are not available.

7 Table III shows the results obtained when diethylenetriamine was used to  
8 make the Mannich bases.

9  
10 Table III

11

Ex.	CO <sub>2</sub> /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
8	0.316	258	0.18	302	11.0
9	NA *	252	0.20	609	14.0
10	0.310	221	0.16	1181	14.0
11	0.336	200	0.19	599	1.3
12	0.489	155	0.16	251	16.0

12  
13 \* Data are not available.

14 Table IV shows the results obtained when ethanol amine was used to make  
15 the Mannich bases. No data were obtained for Example 13 because the  
16 product was too solid.

17

Table IV

Ex.	CO <sub>2</sub> /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
14	0.436	208	0.64	852	0.8
15	0.347	216	0.16	1103	1.5
16	0.390	214	0.17	1374	0.8
17	0.385	211	0.15	1282	2.2
18	0.374	208	0.13	748	0.5
19	0.401	209	<0.05	721	0.5
20	0.392	199	0.13	685	1.2
21	0.384	209	0.15	831	0.3
22	0.400	207	<0.12	1042	0.3
23	0.385	205	<0.04	917	0.3
24	0.382	195	0.19	331	0.8
25	0.390	200	0.19	525	0.9
26	0.413	196	0.13	403	4.0
27	0.369	197	0.16	349	6.8
28	0.369	197	0.16	349	6.8

Table V shows the results obtained when N-phenyl,1,4-phenylene diamine was used to make the Mannich bases.

Table V

Ex.	CO <sub>2</sub> /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
29	0.144	87	0.10	374	8.0

Table VI below lists the components that were varied in Examples 30-46.

50 grams of alkylbenzene sulfonate, wherein the alkyl group on the benzene is 80 percent straight-chain C<sub>20</sub>-C<sub>24</sub> and 20 percent branched-chain C<sub>10</sub>-C<sub>15</sub>, was added to the reaction mixture in Examples 35, 36, 38, 39 and 45.

Ethylene glycol was not added to Example 45.



Table VI

Ex.	Amount of Reaction Components Charge Mole Ratio relative to the Alkylphenol						
	Diethylene- triamine	Ethanol- amine	Monomethyl- amine	1,4- Phenylene- diamine	N,phenyl- 1,4- phenylene- diamine	Ethylene Glycol	Ethylene Carbonate
30	-	-	0.969	0.030	-	0.328	0.394
31	-	-	0.938	0.050	-	0.328	0.473
32	-	-	0.969	0.030	-	0.328	0.315
33	-	-	0.969	0.030	-	0.328	0.473
34	-	-	0.969	0.030	-	0.328	0.474
35	-	-	1.001	0.030	-	0.328	0.474
36	-	-	1.001	0.030	-	0.298	0.358
37	-	-	0.882	0.027	-	0.298	0.358
38	-	-	0.914	0.027	-	0.298	0.358
39	-	-	0.914	0.027	-	0.298	0.358
40	-	0.915	-	0.027	-	0.298	0.376
41	-	0.915	-	0.027	-	0.298	0.376
42	-	0.961	-	0.027	-	0.284	0.358
43	-	0.915	-	0.026	-	0.284	0.358
44	-	0.870	-	0.023	-	0.258	0.358
45	-	1.001	-	0.030	-	0.000	0.358
46	-	0.915	-	0.027	-	0.284	0.358

The results obtained in the above Examples 30-46 in Table VI are given below in Tables VII and VIII.

Table VII shows the results obtained when a combination of two amines, monomethyl amine and 1,4-phenylene diamine, was used to make the Mannich bases.

Table VII

Ex.	CO <sub>2</sub> /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
30	0.413	194	0.19	307	5.6
31	0.425	176	0.17	175	6.0
32	0.411	186	NA *	284	8.4
33	NA *	152	0.23	117	9.2

34	0.397	154	0.19	100	NA *
35	0.446	160	0.23	89	12.3
36	0.414	171	0.27	113	NA *
37	0.455	197	0.23	502	3.2
38	0.450	193	0.26	NA *	3.2
39	0.454	190	<0.06	178	5.0

1

2 \* Data are not available.

3 Table VIII shows the results obtained when a combination of two amines,  
 4 ethanol amine and 1,4-phenylene diamine, was used to make the Mannich  
 5 bases.

6

7

8

Table VIII

Ex.	CO <sub>2</sub> /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
40	0.437	183	0.25	573	NA *
41	0.356	190	0.08	681	5.6
42	0.347	196	0.07	947	2.4
43	0.323	203	0.05	926	2.4
44	0.349	195	0.19	967	2.2
44	0.386	195	0.0	966	4.0
45	0.385	102	0.21	59	10.4
46	0.350	201	0.00	589	4.0

9

10 \* Data are not available.

11

#### Examples A-E

12 The preparation of carbonated, overbased Mannich condensation  
 13 products of alkylphenols using ethylene glycol and carbon dioxide

14

15 Examples A-E experiments were conducted using the same procedure as  
 16 used for Examples 30-46 above, except the ethylene carbonate was replaced  
 17 with ethylene glycol and carbon dioxide for the carbonation of Mannich  
 18 condensation products of alkylphenols. Components kept constant in  
 19 Examples A-E were the Charge Mole Ratio of paraformaldehyde at 1.942, of

1 Ca(OH)<sub>2</sub> at 0.899, and of water at 0.362. Ethylene glycol was added over a  
2 period of 1/2 hour and the carbon dioxide was added over a period of 1 hour.

3

4 In Examples A-D, 50 grams of alkylbenzene sulfonate, wherein the alkyl  
5 group on the benzene is 80 percent straight-chain C<sub>20</sub>-C<sub>24</sub> and 20 percent  
6 branched-chain C<sub>10</sub>-C<sub>15</sub> was added to the reaction mixture.

7

8 Table A below shows the components used in Examples A-E.

9

10  
11

Table A

Ex.	Amount of Reaction Components Charge Mole Ratio relative to the Alkylphenol						
	Diethylene- triamine	Ethanol- amine	Monomethyl- amine	1,4- Phenylene- diamine	N-phenyl- 1,4- phenylene -diamine	Ethylene Glycol	CO <sub>2</sub>
A	-	-	-	0.027	-	0.238	0.655
B	-	-	1.001	0.060	-	0.238	0.818
C	-	-	0.969	0.030	-	0.328	0.788
D	-	-	0.969	0.030	-	0.328	0.788
E	-	-	0.882	0.027	-	0.656	0.358

12

13 The results obtained for Examples A-E are given below in Table B.

14

15

Table B

Ex.	CO <sub>2</sub> /Ca	TBN	Sulfur (weight %)	Viscosity (cSt at 100°C)	Sediment (volume %)
A	0.480	134	0.29	78	NA *
B	0.600	130	0.17	88	NA *
C	0.375	140	0.29	162	8.0
D	0.564	149	0.26	235	7.2
E	0.456	198	0.31	434	7.2

16

17 \* Data are not available.